(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 348 989 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89111915.8**

(51) Int. Cl.4: **B41M 5/26**

(22) Date of filing: **30.06.89**

(30) Priority: **01.07.88 US 214363**

(43) Date of publication of application:
03.01.90 Bulletin 90/01

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

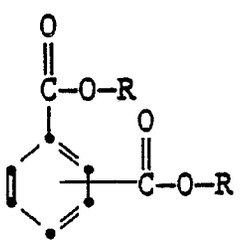
(71) Applicant: **EASTMAN KODAK COMPANY (a New Jersey corporation)**
343 State Street
Rochester New York 14650(US)

(72) Inventor: **Harrison, Daniel Jude c/o EASTMAN KODAK CO.**
Patent Department 343 State Street
Rochester New York 14650(US)
Inventor: **Lum, Kin Kwong c/o EASTMAN KODAK CO.**
Patent Department 343 State Street
Rochester New York 14650(US)

(74) Representative: **Brandes, Jürgen, Dipl.-Chem. Dr. et al**
Thierschstrasse 8
D-8000 München 22(DE)

(54) Phthalate esters in receiving layer for improved dye density transfer.

(57) A dye-receiving element for thermal dye transfer comprising a support having thereon a thermally-transferred dye image in a polymeric dye image-receiving layer containing a phthalate ester having the following formula:



wherein R is a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms or an aralkyl group having from 7 to 12 carbon atoms.

EP 0 348 989 A2

PHTHALATE ESTERS IN RECEIVING LAYER FOR IMPROVED DYE DENSITY TRANSFER

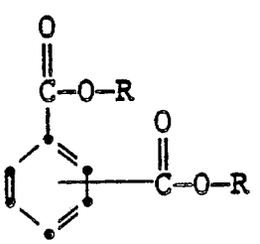
This invention relates to dye-receiving elements used in thermal dye transfer, and more particularly to the use of a phthalate ester in the dye image-receiving layer to improve the dye density transfer.

In recent years, thermal transfer systems have been developed to obtain prints from pictures which have been generated electronically from a color video camera. According to one way of obtaining such prints, an electronic picture is first subjected to color separation by color filters. The respective color-separated images are then converted into electrical signals. These signals are then operated on to produce cyan, magenta and yellow electrical signals. These signals are then transmitted to a thermal printer. To obtain the print, a cyan, magenta or yellow dye-donor element is placed face-to-face with a dye-receiving element. The two are then inserted between a thermal printing head and a platen roller. A line-type thermal printing head is used to apply heat from the back of the dye-donor sheet. The thermal printing head has many heating elements and is heated up sequentially in response to the cyan, magenta and yellow signals. The process is then repeated for the other two colors. A color hard copy is thus obtained which corresponds to the original picture viewed on a screen. Further details of this process and an apparatus for carrying it out are contained in U.S. Patent No. 4,621,271 by Brownstein entitled "Apparatus and Method For Controlling A Thermal Printer Apparatus," issued November 4, 1986.

JP 60/19,138 relates to the use of an image-receiving layer comprising a polycarbonate and a plasticizer. The plasticizers disclosed are all phthalate acid alkyl-esters such as dibutyl phthalate. There is a problem with this compound, however, in that it does not retain its dye density boosting effect upon incubation, as will be shown by comparative tests hereinafter.

It is an object of this invention to provide a compound which would provide increased dye density upon transfer and which would not lose its effect upon keeping.

These and other objects are achieved in accordance with this invention which comprises a dye-receiving element for thermal dye transfer comprising a support having thereon a thermally-transferred dye image in a polymeric dye image-receiving layer, characterized in that the dye image-receiving layer contains a phthalate ester having the following formula:



wherein R is a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms or an aralkyl group having from 7 to 12 carbon atoms.

In the above formula, R may be, for example, phenyl, pyridyl, naphthyl, p-tolyl, p-chlorophenyl, m-(N-methyl sulfamoyl)phenyl, p-methoxyphenyl, benzyl, p-methoxybenzyl, p-chlorobenzyl, etc. In a preferred embodiment of the invention, the phthalate ester is diphenyl phthalate.

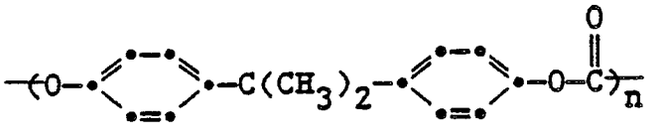
The phthalate ester may be present in the dye image-receiving layer in any amount which is effective for the intended purpose. In general, good results have been obtained when the phthalate ester is present in an amount of from 10 to 100% based on the weight of the material in the dye image-receiving layer.

The polymeric dye image-receiving layer of the dye-receiver of the invention may comprise, for example, a polycarbonate, a polyurethane, a polyester, polyvinyl chloride, poly(styrene-co-acrylonitrile), poly(caprolactone) or mixtures thereof. The dye image-receiving layer may be present in any amount which is effective for the intended purpose. In general, good results have been obtained at a concentration of from 1 to 5 g/m^2.

In a preferred embodiment of the invention, the dye image-receiving layer is a polycarbonate. The term "polycarbonate" as used herein means a polyester of carbonic acid and a glycol or a dihydric phenol. Examples of such glycols or dihydric phenols are p-xylylene glycol, 2,2-bis(4-oxyphenyl)propane, bis(4-oxyphenyl)methane, 1,1-bis(4-oxyphenyl)ethane, 1,1-bis(oxyphenyl)butane, 1,1-bis(oxyphenyl)cyclohexane, 2,2-bis(oxyphenyl)butane, etc.

In another preferred embodiment of the invention, the polycarbonate dye image-receiving layer is a

bisphenol-A polycarbonate having a number average molecular weight of at least 25,000. In still another preferred embodiment of the invention, the bisphenol-A polycarbonate comprises recurring units having the formula

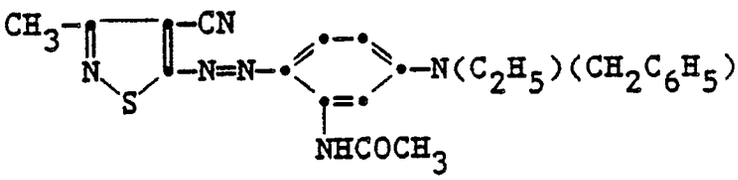


wherein n is from 100 to 500.

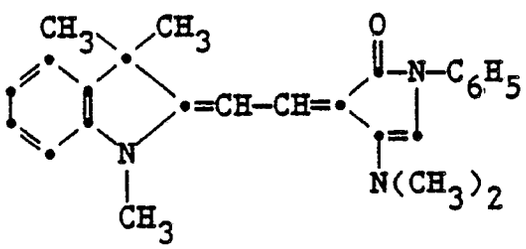
Examples of such polycarbonates include General Electric Lexan@ Polycarbonate Resin #ML-4735 (Number average molecular weight app. 36,000), and Bayer AG Makrolon #5705® (Number average molecular weight app. 58,000). The later material has a T_g of 150°C.

The support for the dye-receiving element of the invention may be a transparent film such as a poly-(ether sulfone), a polyimide, a cellulose ester such as cellulose acetate, a poly(vinyl alcohol-co-acetal) or a poly(ethylene terephthalate). The support for the dye-receiving element may also be reflective such as baryta-coated paper, polyethylene-coated paper, white polyester (polyester with white pigment incorporated therein), an ivory paper, a condenser paper or a synthetic paper such as duPont Tyvek® In a preferred embodiment, polyethylene-coated paper is employed. It may be employed at any thickness desired, usually from 50 μm to 1000 μm.

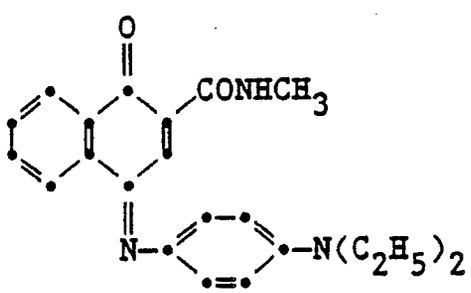
A dye-donor element that is used with the dye-receiving element of the invention comprises a support having thereon a dye layer. Any dye can be 55ed in such a layer provided it is transferable to the dye image-receiving layer of the dye-receiving element of the invention by the action of heat. Especially good results have been obtained with sublimable dyes such as



(magenta)



(yellow)



(cyan)

or any of the dyes disclosed in U.S. Patent 4,541,830. The above dyes may be employed singly or in combination to obtain a monochrome. The dyes may be used at a coverage of from 0.05 to 1 g/m^2 and are preferably hydrophobic.

The dye in the dye-donor element is dispersed in a polymeric binder such as a cellulose derivative. The binder may be used at a coverage of from 0.1 to 5 g/m^2.

The reverse side of the dye-donor element may be coated with a slipping layer to prevent the printing head from sticking to the dye-donor element.

As noted above, dye-donor elements are used to form a dye transfer image. Such a process comprises imagewise-heating a dye-donor element and transferring a dye image to a dye-receiving element as described above to form the dye transfer image.

A thermal dye transfer assemblage of the invention comprises

a) a dye-donor element as described above, and b) a dye-receiving element as described above, the dye-receiving element being in a superposed relationship with the dye-donor element so that the dye layer of the donor element is in contact with the dye image-receiving layer of the receiving element.

The above assemblage comprising these two elements may be preassembled as an integral unit when a monochrome image is to be obtained. This may be done by temporarily adhering the two elements together at their margins. After transfer, the dye-receiving element is then peeled apart to reveal the dye transfer image.

When a three-color image is to be obtained, the above assemblage is formed on three occasions during the time when heat is applied by the thermal printing head. After the first dye is transferred, the elements are peeled apart. A second dye-donor element (or another area of the donor element with a different dye area) is then brought in register with the dye-receiving element and the process repeated. The third color is obtained in the same manner.

The following example is provided to illustrate the invention.

Example 1

A dye-donor of alternating sequential areas of cyan, magenta and yellow dye was prepared by coating on a 6 μm poly(ethylene terephthalate) support:

1) a subbing layer of a titanium alkoxide (duPont Tyzor TBT®)(0.12 g/m^2) from a n-propyl acetate and n-butyl alcohol solvent mixture, and

2) a dye layer containing the cyan dye illustrated above (0.28 g/m^2), the magenta dye illustrated above (0.15 g/m^2) or the yellow dye illustrated above (0.14 g/m^2), and Micropowders, Inc. Fluo-HT® micronized polytetrafluoroethylene(0.05 g/m^2), in a cellulose acetate propionate (2.5% acetyl, 45% propionyl) binder (0.25-0.32 g/m^2) coated from a toluene, methanol and cyclopentanone solvent mixture.

On the back side of the dye-donor was coated:

1) a subbing layer of a titanium alkoxide (duPont Tyzor TBT®)(0.12 g/m^2) from a n-propyl acetate and n-butyl alcohol solvent mixture, and

2) a slipping layer of Petrarch Systems PS513® amino-terminated polysiloxane (0.001 g/m^2); p-toluenesulfonic acid (2.5% of the wt. of the polysiloxane); Emralon 329® (Acheson Colloids Corp.) dry film lubricant of poly(tetrafluoroethylene) particles in a cellulose nitrate resin binder (0.54 g/m^2); and BYK-320® (BYK Chemie, USA) copolymer of a polyalkylene oxide and a methyl alkylsiloxane (0.002 g/m^2), coated from a n-propyl acetate, toluene, isopropyl alcohol and n-butyl alcohol solvent mixture.

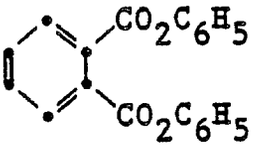
A control dye-receiving element was prepared by coating the following layers in the order recited on a titanium dioxide-pigmented polyethylene-overcoated paper stock:

1) Subbing layer of poly(acrylonitrileco-vinylidene chloride-co-acrylic acid) (14:79:7 wt. ratio) (0.08 g/m^2) coated from 2-butanone, and

2) Dye-receiving layer of Makrolon 5705® (Bayer AG Corporation) polycarbonate resin (2.9g/m^2), FC-431® surfactant (3M Corp.) (0.016 g/m^2) and Tone PCL-700® polycaprolactone (Union Carbide) in the amount stated in the Table, coated from methylene chloride.

Another control element was prepared similar to the one above except that it contained di-n-butyl phthalate (Kodak L&R Products) instead of the polycaprolactone.

A dye-receiving element according to the invention was prepared similar to the control elements except that instead of the polycaprolactone it contained diphenyl phthalate:



The dye side of the dye-donor element strip approximately 10 cm x 13 cm in area was placed in contact with the dye image-receiving layer of the dye-receiver element of the same area. The assemblage was clamped to a stepper-motor driven mm diameter rubber roller and a TDK Thermal Head (No. L-231) (thermostatted at 26° C) was pressed with a force of 8.0 pounds (3.6 kg) against the dye-donor element side of the assemblage pushing it against the rubber roller.

The imaging electronics were activated causing the donor/receiver assemblage to be drawn between the printing head and roller at 6.9 mm/sec. Coincidentally, the resistive elements in the thermal print head were pulsed for 29 µsec/pulse at 128 µsec intervals during the 33 msec/dot printing time. A stepped density image was generated by incrementally increasing the number of pulses/dot from 0 to 255. The voltage supplied to the print head was approximately 23.5 volts, resulting in an instantaneous peak power of 1.3 watts/dot and a maximum total energy of 9.6 mjoules/dot. Individual color stepped images were obtained by printing from the three dye-donors.

The amount of dye transferred into the receiver was calculated by measuring the % dye remaining in the dye-donor using a Status A transmission densitometer and subtracting that % from 100. Surface gloss or lack thereof was visually estimated. The following results were obtained:

Table 1

Receiving Layer Addendum (g/m^2)		% Dye Transfer			Surface Gloss
		Blue	Green	Red	
Polycaprolactone	(0)	42	32	35	Yes
Polycaprolactone	(0.44)	49	34	38	Yes
Polycaprolactone	(0.87)	48	35	36	Yes
Polycaprolactone	(1.74)	46	49	63	Yes
Polycaprolactone	(2.34)*	70	55	56	Hazy
Dibutyl phthalate	(0.87)	66	54	50	Yes
Dibutyl phthalate	(1.74)	81	75	71	Yes
Dibutyl phthalate	(2.37)	84	79	76	Yes
Diphenyl phthalate	(0.44)	59	44	47	Yes
Diphenyl phthalate	(0.87)	64	51	47	Yes
Diphenyl phthalate	(1.74)	78	65	57	Yes
Diphenyl phthalate	(2.37)	81	72	70	Yes

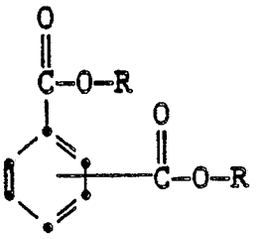
*Equivalent to 45% polycaprolactone and 55% polycarbonate

The above results show that both dibutyl phthalate and diphenyl phthalate are more effective in increasing dye transfer efficiency than polycaprolactone at a given level without affecting surface gloss.

However, in a similar experiment, the dibutyl phthalate lost its effectiveness when the dye-receiver was incubated.

Claims

1. A dye-receiving element for thermal dye transfer comprising a support having thereon a thermally-transferred dye image in a polymeric dye image-receiving layer, characterized in that said dye image-receiving layer contains a phthalate ester having the following formula:



wherein R is a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms or an aralkyl group having from 7 to 12 carbon atoms.

2. The element of Claim 1 characterized in that R is phenyl.

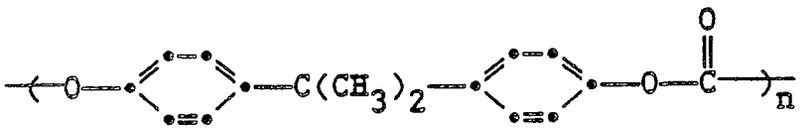
3. The element of Claim 1 characterized in that said ester is diphenyl phthalate.

4. The element of Claim 1 characterized in that said phthalate is present in an amount of from 10 to 100% based on the weight of the dye image-receiving layer.

5. The element of Claim 1 characterized in that said support is poly(ethylene terephthalate).

6. The element of Claim 1 characterized in that said dye image-receiving layer is a bisphenol-A polycarbonate having a number average molecular weight of at least 25,000.

7. The element of Claim 6 characterized in that said bisphenol-A polycarbonate comprises recurring units having the formula



wherein n is from 100 to 500.

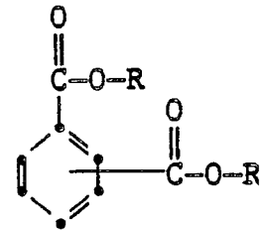
8. A thermal dye transfer assemblage comprising:

a) a dye-donor element comprising a support having thereon a dye layer, and

b) a dye-receiving element comprising a support having thereon a polymeric dye image-receiving layer,

said dye-receiving element being in a superposed relationship with said dye-donor element so that said dye layer is in contact with said dye image-receiving layer,

characterized in that said dye image-receiving layer contains a phthalate ester having the following formula:



wherein R is a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms or an aralkyl group having from 7 to 12 carbon atoms.

9. The assemblage of Claim 8 characterized in that R is phenyl.

10. The assemblage of Claim 8 characterized in that said ester is diphenyl phthalate.